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**(54) Photographic materials for use in redox amplification and process**

(57) A photographic silver halide colour material eg paper, suitable for use in redox amplification comprises a support bearing one or more emulsion layers, at least one of said layers containing a sulphur-containing anti-fogging agent for example mercaptotetrazole, the amount of said agent being effective to reduce fog but not more than 0.5mg/m<sup>2</sup>, preferably not more than 0.3mg/m<sup>2</sup>. Preferably the antifogging agent is incorporated into a blue or green sensitive layer. Using the present invention a redox amplification process can be carried out at temperatures up to 37°C with acceptable fog control.

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**Description****Field of the Invention**

5 This invention relates to photographic silver halide colour materials and in particular to low silver colour materials suitable for use in redox amplification processing.

**Background of the Invention**

10 Redox amplification processes have been described, for example in British Specifications Nos. 1,268,126; 1,399,481; 1,403,418; and 1,560,572. In such processes colour materials are developed to produce a silver image (which may contain only small amounts of silver) and treated with a redox amplifying solution (or a combined developer/amplifier) to form a dye image. The development and amplification solutions can be separate or combined. The combined solution, which is more common, is known as developer-amplifier and contains a reducing agent, for example a colour developer, 15 and an oxidizing agent, for example hydrogen peroxide. The latter oxidizes the colour developing agent under the catalytic influence of the developed silver image. The oxidized colour developer so formed reacts further with a colour coupler coated in the same or in an adjacent layer to produce an image.

In a typical arrangement the emulsion layers of a colour paper photographic material comprise substantially pure silver chloride. One feature of a redox system is that since silver acts as a catalyst for amplification it is possible to use only 20 very low levels of coated silver chloride. This has benefits for effluent reduction during processing and also permits the elimination of the bleach solution. Undeveloped silver halide is fixed from the coating, but developed silver is left in the coating after exposure and processing.

**Problem to be solved by the Invention**

25 It has been previously reported that the image developed in photographic systems sometimes lacks clarity and this loss of clarity has been described as fogging. To combat this problem it has been proposed to employ compounds which have become known as antifogging compounds. Many antifogging compounds are known including mercaptotetrazoles. One of these is 1-phenyl-5-mercaptotetrazole (PMT, 1-phenyl-2-tetrazoline-5-thione) and is widely used, see for 30 example, F.W. Mueller; Review of mechanisms of Emulsion Stabilizers and Antifogging Agents, International Congress of Photographic Science, Tokyo 1967, Ed S. Kikuchi. Focal Press 1970). More specifically PMT is used in the magenta layer of EKTACOLOR™ papers.

In redox systems it has been previously reported that sulphur-containing antifogging agents which are effective in conventional colour paper systems, poison the silver catalyst. When attempts have been made to use these compounds it 35 has been found that, although they have a powerful antifogging action, amplification of the image is suppressed, leading to very little dye image. This problem has been described in US Patent No 4,088,494 and proposes as a solution incorporating a heterocyclic compound having at least one mercapto group, at least two aza nitrogen atoms and a pKa of not more than 7.6 into a sulphur sensitized silver halide photographic emulsion containing at least 80% silver bromide or chloride, where substantially all of the silver halide particles present are of cubic crystal form.

40 However the general view of those skilled in the art has been that because sulphur poisons the silver catalyst, sulphur-containing antifoggants should be avoided in redox systems. It has therefore been proposed to use as antifogging agents, compounds that do not contain sulphur. Examples of these are disclosed in GB Patent Nos 1,539,804 and 1,549,295 which describe respectively, various nitrogen containing heterocyclic compounds and polymeric compounds. Further non mercapto compounds are described in U.S. Patent No 4,062,684; GB 1,580,716; J58/137,837 and DE 45 3,228,192.

It has now been found, unexpectedly, that sulphur-containing compounds for example mercaptotetrazoles, when used in small and carefully controlled amounts, are effective antifogging agents in redox systems without significantly reducing the amplification.

**Summary of the Invention**

50 According to the present invention there is provided a photographic silver halide colour material suitable for use in redox amplification said material comprising a support bearing one or more emulsion layers, at least one of said layers containing a sulphur-containing antifogging agent, the amount of said agent being effective to reduce fog but not more 55 than 0.5mg/m<sup>2</sup> preferably not more than 0.3mg/m<sup>2</sup>.

The invention also provides a process for the redox development of an imagewise exposed photographic material which process comprises developing the photographic material in a redox developer/amplifier solution and wherein the photographic material contains in an emulsion layer an effective amount of a sulphur-containing antifogging agent but not more than 0.5mg/m<sup>2</sup> preferably not more than 0.3mg/m<sup>2</sup>.

According to a further aspect of the present invention there is provided a process for the preparation of a photographic silver halide colour material suitable for use in redox amplification which process comprises forming a plurality of layers on a support and incorporating into the blue or green sensitive layer a sulphur-containing antifogging agent in an amount effective to reduce fogging but less than  $0.5\text{mg/m}^2$ , preferably less than  $0.3\text{mg/m}^2$ .

### Advantageous Effect of the Invention

The advantage of the present invention is that it enables mercaptotetrazoles and other sulphur-containing antifogging agents to be used in redox development systems without significantly reducing the amplification. In a multilayer coating, fog control in all records can be achieved by the placement of a mercaptotetrazole in the yellow and/or magenta layers and specifically in dispersion melts for improved effectiveness.

### Detailed Description of the Invention

The sulphur-containing antifogging agent used in the present invention can be any of those known in the art as antifogging agents and is preferably a heterocyclic organic molecule containing nitrogen in a ring.

Preferably the sulphur is in a mercapto group. Examples of suitable compounds are mercaptotetrazoles, mercaptotriazoles, mercaptodiazoles, mercaptobenzothiazoles and mercaptobenzimidazoles.

A mercaptotetrazole is preferred and may be substituted in the 1-position by a monovalent organic group for example a hydrocarbyl group which may be aliphatic or aromatic eg phenyl.

Suitable sulphur-containing antifogging agents are described in United States Patent No 4,088,494. The antifogging agent may be used in a blocked form, that is to say, in a form in which it is combined with a blocking group, the latter being removable in the presence of peroxide. The blocking and subsequent release of the antifogging agent may be effected as described in European Patent Application No 547,707A.

It is not however preferred to provide the antifogging agent in the photographic material in a blocked form and it may more conveniently be provided in an active form.

For use in the present invention an effective amount ie providing a useful antifogging effect, of antifogging agent will be at least  $0.05\text{mg/m}^2$  and will usually be at least  $0.10\text{mg/m}^2$ . Typically the amount of antifogging agent is from about one tenth to about one quarter of the amount used in conventional colour papers.

Conveniently the redox developer/amplifier solution used in the present invention comprises a colour developing agent, hydrogen peroxide or a compound which provides hydrogen peroxide and hydroxylamine or a salt thereof.

The colour developing agent may be any of those known in the art, for example, the p-phenylene diamines eg N N N'N'-tetramethyl phenylene diamine. Convenient concentration ranges are:

hydrogen peroxide from 0.5 to 15 ml/l (as 30% w/w solution),  
hydroxylamine or a salt thereof from 0.25 to 8 g/l (as hydroxylamine sulphate),

and wherein the pH is in the range from 10.5 to 12.5.

The concentration range of the hydrogen peroxide is preferably from 0.5 to 7 ml/l and especially from 0.5 to 2 (as 30% w/w solution).

The concentration range of the hydroxylamine component is from 0.5 to 4 and especially from 0.5 to 2 g/l (as hydroxylamine sulphate).

The pH is preferably in the range 11 to 11.7 and especially from 11 to 11.4.

The composition is preferably free of any compound that forms a dye on reaction with oxidised colour developer.

The relative proportions of hydrogen peroxide (as ml/l of a 30% w/w solution) and hydroxylamine compound (as g/l hydroxylamine sulphate) need to be balanced to give the required result.

The photographic material may be first subjected to a development step with a developer solution containing no peroxide or other oxidising agent before the redox amplification. Alternatively, the development and amplification may be combined in a single step using a combined developer/amplifier solution.

The process of redox amplification is conventionally carried out at  $32^\circ\text{C}$ . The process of the present invention can however be carried out at temperatures up to  $37^\circ\text{C}$  with acceptable fog control.

The colour photographic material to be processed may be of any type but will preferably contain low amounts of silver halide. Preferred total silver halide coverages are in the range 6 to 300, preferably 10 to 200  $\text{mg/m}^2$  and particularly 10 to 100  $\text{mg/m}^2$  (as silver).

A particular application of redox amplification is in the processing of silver chloride colour paper, for example, paper comprising at least 85 mole % silver chloride, especially such paper with low silver levels for example levels below  $30\text{mg/m}^2$  preferably below  $20\text{mg/m}^2$ .

The material may comprise the emulsions, sensitisers, couplers, supports, layers, additives, etc. described in Research Disclosure, December 1978, Item 17643, published by Kenneth Mason Publications Ltd, Dudley Annex, 12a

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In a preferred embodiment the photographic material to be processed comprises a resin-coated paper support and the emulsion layers comprise more than 80%, preferably more than 90% silver chloride and are more preferably composed of substantially pure silver chloride.

The photographic materials can be single colour materials or multicolour materials. Multicolour materials contain dye image-forming units sensitive to each of the three primary regions of the spectrum. Each unit can be comprised of a single emulsion layer or of multiple emulsion layers sensitive to a given region of the spectrum. The layers of the materials, including the layers of the image-forming units, can be arranged in various orders as known in the art.

A typical multicolour photographic material comprises a support bearing a yellow dye image-forming unit comprised of at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler, and magenta and cyan dye image-forming units comprising at least one green- or red-sensitive silver halide emulsion layer having associated therewith at least one magenta or cyan dye-forming coupler respectively. The material can contain additional layers, such as filter layers.

The invention also provides a process for the preparation of a photographic silver halide colour material suitable for use in redox amplification.

The preparation of photographic papers conventionally involves coating the paper with a number of photographic materials in a plurality of coatings to form separate layers and sometimes up to seven layer may be applied.

It is the usual practice to prepare the photosensitive coating material which is to provide one of the layers as two separate components which are mixed together either immediately or shortly before the coating operation. One component which is normally referred to as the emulsion comprises a silver halide, usually silver chloride, gelatin and water together with optional ingredients such as chemical sensitizers, spectral sensitizers and antifogging agents. Although this may not be truly an emulsion in the physical-chemical sense, the term has been universally accepted in the photographic art.

The other component comprises an imaging coupler in a finely divided form in a gelatin medium. As initially prepared, the emulsion and the dispersion are too concentrated to be used to coat paper and the usual procedure is to dilute them with water and gelatin. After dilution they are usually solid at room temperature ie about 20°C but melt at about 25°C. In the melted states they are referred to as the emulsion melt and the dispersion melt respectively.

The process for the preparation of the photographic materials according to the present invention may comprise forming an emulsion melt and a dispersion melt for coating the base and incorporating the sulphur-containing antifogging agent into either the emulsion melt or the dispersion melt used to form a green or blue sensitive layer of the photographic material.

The invention is illustrated by the following Examples.

The compound 1-phenyl-5-mercaptotetrazole was incorporated into monochrome single-layer or full colour multi-layer coatings in the form of a 0.5% by weight solution in ethanol. The antifoggant solution was added to either the emulsion melt or to the dispersion melt of the layer of interest. The prepared coatings were given an exposure at 0.1 second on the DF1 sensitometer, using neutral and separation step-wedges appropriately colour balanced for colour-negative paper. The processing used a redox-amplification procedure, employing the redox-amplifier formulation and process protocol given in Table 1 to 3. Tables 1 and 2 give the formulations for 1.0 litres of redox processing solutions.

Table 1

DEVELOPER-AMPLIFIER	
Component	Concentration.
AC5	0.6g
AC8	2.0ml
K <sub>2</sub> HPO <sub>4</sub> ·3H <sub>2</sub> O	40.0g
KBr	1.0mg
KCl	0.5g
CDS	0.3g
KOH (50%)	10.0ml
HAS	1.0g
CD3	4.5g
H <sub>2</sub> O <sub>2</sub> (30%)	2.0ml
pH	11.4
Temperature	32°C
Time	45 seconds

Table 2

FIXER	
Component	Concentration
Na <sub>2</sub> SO <sub>3</sub>	100.0g
CH <sub>3</sub> COOH (glacial)	50.0ml
NaOH (50%)	70.0ml
pH	7.0
Temperature	32°C
Time	30 seconds

Table 3

PROCESS SEQUENCE	
Develop-amplify	45 seconds
Fix	30 seconds
Wash	60 seconds

AC5 is a 60% aqueous solution of 1-hydroxy-ethylidene-1,1-diphosphonic acid.  
 AC8 is a 40% aqueous solution of the penta sodium salt of diethylene triamine penta acetic acid.  
 CDS is catechol disulphonate  
 HAS is hydroxylamine sulphate

CD3 is N-2-(4 amino-N-ethyl-m-toluidino)ethyl methanesulphonamide sesquisulphate hydrate.

The separation and/or neutral wedges on the processed material were measured with a densimeter and appropriate sensitometric parameters calculated.

#### 5 Example 1. Yellow single colour records.

Yellow monochrome coatings were made by dual melting a blue sensitive emulsion melt together with EKTACOLOR™ yellow dispersion melts which were prepared either with or without the compound of interest. The emulsion was similar to that used in EKTACOLOR™ paper except for having a reduced cubic grain edge length of 0.45 micrometres. The silver laydown was 31mg/m<sup>2</sup>. Other component laydowns were as used in EKTACOLOR™ paper. A common supercoat similar to that employed in EKTACOLOR™ was coated over the yellow layer. Table 4 gives the details of the quantity of PMT used together with sensitometric data for the coatings when processed in a redox amplifier formulation.

15 Table 4

Coating No.	PMT mg/m <sup>2</sup>	Dmin	Dmax	Contrast	Inertial Speed
S19036	0	0.092	2.250	3.591	83.3
S19043	0	0.092	2.255	3.627	84.1
S19044	0.2 YD	0.071	2.259	3.374	83.4

It can be seen that the use of PMT gives a 23% reduction in blue minimum density (fog) with no loss in maximum density or speed and only a 6.5% reduction in contrast, which is judged to be acceptable.

#### 25 Example 2. Magenta single colour records.

Magenta monochrome coatings were made by dual-melting an EKTACOLOR™ magenta dispersion melt together with green-sensitive emulsion melts which were prepared either with or without the compound of interest at a series of levels.

The emulsion was similar to that used in EKTACOLOR™ paper, except for having a reduced cubic grain edge length of 0.27micrometres. The silver laydown was 16mg/m<sup>2</sup>. Other component laydowns were as used in EKTACOLOR™ paper. A common supercoat similar to that employed in EKTACOLOR™ was coated over the magenta layer. Table 5 gives details of the quantities of PMT used, together with sensitometric data for the coatings when processed in a redox amplifier solution.

40 Table 5

Magenta Single Colour Records.					
Coating No.	PMT mg/m <sup>2</sup>	Dmin	Dmax	Contrast	Inertial Speed
S18709	0	0.132	2.623	3.612	88.4
S18717	0.1 ME	0.108	2.641	4.085	84.1
S18718	0.3 ME	0.106	2.531	3.385	88.8
S18719	1.0 ME	0.115	0.834	0.980	79.5

It can be seen that the use of PMT in magenta monochromes at levels between 0.1 and 0.3mg/m<sup>2</sup> gives a substantial reductions in Dmin without any important changes in other sensitometric parameters. However, when the level is increased to 1.0mg/m<sup>2</sup>, close to what is used in the prior art materials, a serious degradation of imaging performance is observed.

#### 55 Example 3. Full-color multilayer coatings.

Comparison of PMT in emulsion and in dispersion melt, and in yellow and magenta layers.

Multilayer coatings were made using the same structure and components as EKTACOLOR™ paper, except for the

following emulsion changes which were implemented to make the coatings suitable for a redox amplification process. Emulsion grain cubic edge lengths and silver laydowns were reduced in all three records to respectively: yellow 0.45 micrometres and 28mg/m<sup>2</sup>; magenta 0.27 micrometres and 19mg/m<sup>2</sup>; cyan 0.29 micrometres and 14mg/m<sup>2</sup>. Table 6 gives details of the level and placement of PMT which was variously positioned in the yellow emulsion or dispersion then additionally in the magenta or dispersion. The sensitometric data for the coatings when processed in a redox amplifier formulation is also given.

Table 6

Full Colour Multilayer Coatings. PMT in emulsion vs dispersion melt; yellow vs magenta layers.					
Coating	PMT mg/m <sup>2</sup>	Dmin	Dmax	Contrast	Inertial speed
S19681 R	0.0	0.114	2.565	3.888	139.9
G		0.127	2.493	3.855	142.9
B		0.095	2.236	2.477	148.4
S19680 R		0.110	2.554	3.765	140.1
G		0.111	2.423	3.575	143.0
B	0.2 YE	0.089	2.236	2.448	142.5
S19682 R		0.110	2.587	3.728	139.9
G		0.111	2.509	3.700	141.1
B	0.2 YD	0.092	2.207	2.634	143.6
S19683 R		0.105	2.479	3.540	138.5
G	0.2 MD	0.106	2.393	3.442	139.2
B	0.2 YD	0.085	2.076	2.498	141.6
S19684 R		0.105	2.521	3.689	138.8
G	0.2 ME	0.106	2.044	1.788	111.4
B	0.2 YD	0.084	2.046	2.418	139.3

The abbreviations YD, MD stand for yellow dispersion, magenta dispersion etc. In the case of YD it means that the antifogging agent was added to the yellow dispersion melt.

It can be seen that incorporation of PMT in either the yellow emulsion or yellow dispersion is equally effective in reducing Dmin in all records; the other sensitometric parameters are relatively unaffected by the position in the yellow melts. When PMT is in the yellow dispersion and additionally in the magenta dispersion or emulsion there are further reductions in Dmin in all layers but now at the expense of sensitometric losses in some cases. This is particularly so for the magenta emulsion incorporation. The results suggest that a total PMT laydown of 0.4mg/m<sup>2</sup> is somewhat high for a multilayer coating and that the magenta emulsion is best left untreated.

#### Example 4

Multilayer coatings were made as in Example 3 except that the PMT was confined to the dispersion melts. Its level and distribution between yellow, magenta and cyan records was varied. Table 7 gives details of these changes and the resulting sensitometric effects.

Table 7

Coating	PMT mg/m <sup>2</sup>	Dmin	Dmax	Contrast	Inertial Speed
S20366 R	0.0	0.170	2.763	4.395	146.9
G		0.197	2.576	3.900	143.4
B		0.167	2.073	2.441	148.9
S20368 R		0.122	2.777	4.451	146.7
G		0.129	2.594	3.978	142.6
B	0.2 YD	0.111	2.123	2.502	146.0
S20370 R		0.121	2.702	4.084	146.3
G	0.2 MD	0.130	2.567	3.806	141.3
B		0.113	2.138	2.533	144.8
S20372 R		0.116	2.710	4.242	145.4
G	0.1 MD	0.124	2.584	3.927	141.0
B	0.1 YD	0.106	2.081	2.466	144.9
S20375 R	0.05 CD	0.117	2.681	4.000	144.9
G	0.05 MD	0.125	2.543	3.746	141.3
B	0.10 YD	0.108	2.039	2.428	144.6
S20367 R		0.117	2.737	4.310	144.6
G		0.124	2.541	3.843	140.6
B	0.30 YD	0.106	2.028	2.380	143.6
S20373 R	0.10 CD	0.114	2.264	3.179	146.2
G	0.10 MD	0.124	2.545	3.714	140.1
B	0.10 YD	0.106	2.013	2.375	143.9

It can be seen from these results that coatings S20368, -70, -72, -75 which have a total PMT laydown of 0.2mg/m<sup>2</sup> show that the variation with half of the total in each of the yellow and magenta dispersion melts (coating-72) is marginally preferable to the other coatings for Dmin in all records and substantially superior to coating S20366 which has no PMT. Coating -75 with PMT in all dispersions shows some evidence of red Dmax and contrast losses. When the higher level of 0.3mg/m<sup>2</sup> is employed (coatings - 67, -73), there is no further improvement in Dmin and the coating with the even distribution (-73) shows losses in red Dmax and contrast. The results suggest that the PMT should be confined to the yellow and magenta dispersion melts with a level at or below 0.3mg/m<sup>2</sup>.

#### Example 5 Full colour multilayer coatings, high temperature processing.

Multilayer coatings were made as in Example 3. The redox development-amplification was conducted at 37°C instead of the normal 32°C. Table 8 gives details of the PMT levels and the resulting sensitometric data.

Table 8

Full-colour Multilayer Coatings. Higher Temperature Development-Amplification.					
Coating	PMT mg/m <sup>2</sup>	Dmin	Dmax	Contrast	Inertial speed
S18408 R	0.0	0.267	2.494	3.448	134.2
G		0.400	2.443	3.232	130.9
B		0.342	2.155	2.670	145.9
S18822 R	0.0	0.306	2.618	3.978	133.9
G		0.436	2.271	2.079	112.2
B		0.288	1.759	1.976	137.3
S18826 R		0.124	2.589	3.963	140.1
G	0.2ME	0.129	2.322	2.618	133.8
B		0.109	1.817	2.212	145.7
S18831 R		0.113	2.581	3.897	140.8
G	0.2ME	0.115	2.321	2.581	133.9
B		0.100	1.960	2.382	145.1
S19683 R		0.111	2.470	3.608	139.4
G	0.2MD	0.117	2.373	3.455	139.4
B	0.2YD	0.095	1.924	1.935	138.9

It can be seen from the above results that the coatings without PMT showed unacceptably high fog levels at this temperature. Incorporation of PMT brought the Dmin values down to levels comparable with those encountered in Examples 3 and 4. Coating S19683 also appears in Table 6 so a direct comparison of 37°C against 32°C processing can be made. The Dmin values are only a little higher, and still acceptable, at the higher temperature.

#### Claims

1. A photographic silver halide colour material suitable for use in redox amplification said material comprising a support bearing one or more emulsion layers, at least one of said layers containing a sulphur-containing antifogging agent, the amount of said agent being effective to reduce fog but not more than 0.5mg/m<sup>2</sup> preferably not more than 0.3mg/m<sup>2</sup>.
2. A photographic material as claimed in claim 1 wherein the sulphur-containing antifogging agent is an organic heterocyclic compound containing nitrogen in a ring.
3. A photographic material as claimed in claim 2 wherein the antifogging agent is a mercaptotetrazole, mercaptotriazole, mercaptooxadiazole, mercaptobenzothiazole or mercaptobenzimidazole.
4. A photographic material as claimed in any one of the preceding claims wherein the amount of antifogging agent is at least 0.05mg/m<sup>2</sup>.
5. A photographic material as claimed in any one of the preceding claims wherein the silver halide is at least 85 mole % silver chloride.
6. A photographic material as claimed in any one of claims 1 to 5 wherein the material contains less than 200mg/m<sup>2</sup> of silver, preferably less than 35mg/m<sup>2</sup>.
7. A photographic material as claimed in any one of the preceding claims wherein the sulphur-containing antifogging

agent is incorporated into a blue or green sensitive layer.

5 8. A process for the redox development of an imagewise exposed photographic material which process comprises developing the photographic material in a redox developer/amplifier solution and wherein the photographic material contains in an emulsion layer an effective amount of a sulphur-containing antifogging agent but not more than 0.5mg/m<sup>2</sup>, preferably not more than 0.3mg/m<sup>2</sup>.

9. A process as claimed in claim 8 wherein the antifogging agent is present in a blue or green sensitive layer.

10 10. A process as claimed in claim 8 or 9 wherein the amount of the antifogging agent is at least 0.05mg/m<sup>2</sup>.

11. A process as claimed in any one of claims 8 to 10 wherein the process is carried out at up to 37°C.

15 12. A process for the preparation of a photographic silver halide colour material suitable for use in redox amplification which process comprises forming a plurality of layers on a support and incorporating into the blue or green sensitive layer a sulphur-containing antifogging agent in an amount effective to reduce fogging but less than 0.5mg/m<sup>2</sup>, preferably less than 0.3mg/m<sup>2</sup>.

20 13. A process as claimed in claim 12 which comprises forming an emulsion melt and a dispersion melt for coating the base and wherein the sulphur-containing antifogging agent is incorporated into either the emulsion melt or the dispersion melt used to form a green or blue sensitive layer of the photographic material.

14. A process as claimed in claim 12 or 13 wherein the amount of antifogging agent is at least 0.05mg/m<sup>2</sup>.

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